Background removal in scanning tunneling spectroscopy of single atoms and molecules on metal surfaces

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Scanning tunneling spectroscopy has developed into a powerful spectroscopic technique that has found wide application in the atomic scale characterization of the electronic properties of clean surfaces as well as adsorbates and defects at surfaces. However, it still lacks the standard methods for data treatment and removal of artifacts in spectra as they are, e.g., common in photoemission spectroscopy. The properties of the atomic scale tip apex—the probe of the instrument—tend to introduce spurious background signals into tunneling spectra. We present and discuss two methods which permit to extract tip-independent information from low temperature tunneling spectra acquired on single atoms and molecules on single crystal surfaces by background subtraction. The methods rely on a characterization of the tip on the clean metal surface. The performance of both methods is demonstrated and compared for simulated and experimental tunneling spectra. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2907533]

I. INTRODUCTION

The development of low temperature scanning tunneling microscopes (STMs) has enabled scanning tunneling spectroscopy (STS) on single atoms and molecules at metal surfaces.[1,2] Low temperatures are a prerequisite, on the one hand, for the stability of the tunneling junction and the tip and, on the other hand, define the limit of the energy resolution. A variety of new and challenging experiments have been enabled by the unique spatial and spectroscopic resolution of STS, which allows to map electronic features and vibrational excitations with atomic resolution. The main disadvantage of STS, however, is that the chemistry and shape of the apex of the tip—the "detector" of the STM—can hardly be controlled. Although several recipes have been proposed (see, e.g., Ref. 3 and references therein), the very end of the tip will still vary considerably from tip to tip and may even change during a measurement. This is why it is essential to develop standard methods for the treatment of STS spectra as they exist already for a long time for photoemission spectra, see, e.g., Refs. 4 and 5. Possibilities to extract the local density of states (LDOS) from tunneling spectra have already been addressed,[6–10] especially how the influence of the transmission through the tunneling barrier can be eliminated. Recently, the normalization of spectra taken on different spots on the surface but with the same tip has been discussed.[7] Background removal for STS spectra which "calibrates" the tip on a spot of the surface with a known LDOS has been proposed and employed in the specific context of inelastic tunneling spectroscopy (IETS).[2,11]

The basic idea of the background subtraction schemes presented here is to characterize the LDOS of the tip on a clean spot of the surface and remove features due to the tip LDOS from the spectrum acquired with the same tip on the object of interest. Thereby, the need to prepare a certain quality tip LDOS is alleviated. Of course, this will only work if the LDOS of the clean surface is known.

This paper is organized as follows: first, the background subtraction schemes will be introduced and their limits discussed, then, we will show their application to simulated STS spectra and finally how they perform on experimental data.

Our discussion of STS is focused on $dI/dV(V)$ spectroscopy, where the spectrum is recorded in open-feedback loop conditions, i.e., at constant tip-sample distance. We start from the expression for the tunneling current I between tip and sample as derived by Lang,[8] which is approximated by

$$I(V) \propto \int_{-\infty}^{\infty} \rho_S(E)\rho_t(E-eV)\mathcal{T}(E,V,s)w(E,V,T)dE. \quad (1)$$

Here, ρ_S is the LDOS of the sample at the point of interest, ρ_t that of the tip, and $w(E,V,T)=f(E-eV,T_t)-f(E,T_s)$ contains the Fermi functions of tip and sample, respectively. The transmission coefficient of the tunneling barrier[8]

$$\mathcal{T}(E,V,s) = \exp\left(-2s\sqrt{\frac{m}{\hbar^2}(\Phi_s + \Phi_t - 2E + eV)}\right) \quad (2)$$

depends further on the tip-sample distance s and the work functions Φ_t and Φ_s of tip and sample, respectively. In the following, we assume that sample and tip temperature are the same, however, it should be noted that the spectroscopic resolution is determined by the temperature of the tip. We will also assume that the tunneling bias V is small compared to the work functions of tip and sample. In this case, the transmission coefficient is to a first approximation independent of
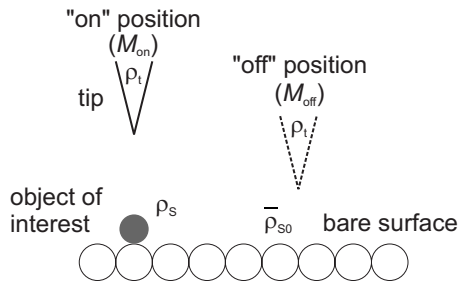

FIG. 1. Sketch of the measurement geometry of on and off spectra and assignment of the symbols.

the bias voltage. This implies that the validity of the discussed background removal schemes is limited to cases where the transmission is comparable for different tips and at the different places of interest on the sample and nearly energy independent, which might not be the case with an adsorbate attached to the tip or if the overlap between tip and sample orbitals varies strongly between the sample surface and the object under investigation. Furthermore, for spectral features whose width Γ is large compared to the thermal broadening, the Fermi functions can be approximated by a step function, i.e., $f(E) = 1 - \theta(E)$. For measurements at liquid helium temperature, this approximation puts a lower limit of $k_B T \sim 0.4$ meV to Γ. With these approximations, Eqs. (1) and (2) simplify to

$$I(V) \propto \int_0^{eV} \rho_S(E)\rho_t(E - eV)dE. \tag{3}$$

Typically, spectra are recorded using a lock-in technique which introduces additional broadening. This effect will be ignored in the following derivation, an assumption which is valid as long as the lock-in modulation is small compared to the width of the spectral features under consideration. If the lock-in modulation is comparable to the energetic width of the spectral features to be resolved, it can be easily accounted for, as discussed by Klein *et al.*[12] The $dI/dV(V)$ signal can be calculated from the derivative of Eq. (3). We will denote the $dI/dV(V)$ spectrum measured on the object under investigation M_{on} and the spectrum of the clean surface M_{off}. The setup is sketched in Fig. 1. In order to recover the spectrum of the sample, the LDOS of the tip is characterized on a clean spot of the surface. For simplicity, the LDOS of the clean sample $\rho_{S0}(E) = \bar{\rho}_{S0}$ is assumed to be constant. Then, the "off" spectrum M_{off} is given by

$$M_{off}(V) = C_{off}\bar{\rho}_{S0}\rho_t(-eV), \tag{4}$$

where the transmission coefficient and constants are absorbed in C_{off}. The off spectrum gives direct access to the LDOS of the tip ρ_t. Placing the same tip on top of the object of interest gives the "on" spectrum M_{on}

$$M_{on}(V) = C_{on}\left[\rho_S(eV)\rho_t(0) - \int_0^{eV} \rho_S(E)\frac{d}{dE}\rho_t(E - eV)dE\right]. \tag{5}$$

Again, the transmission probability and proportionality constants are summarized in C_{on}. Eq. (5) can be rewritten by partial integration to yield

$$M_{on}(V) = C_{on}\left[\rho_S(0)\rho_t(-eV) + \int_0^{eV} \frac{d}{dE}\rho_S(E)\rho_t(E - eV)dE\right]. \tag{6}$$

II. SUBTRACTION

We use a Taylor expansion for $\rho_t(E)$ around $E = 0$,

$$\rho_t(E) = \rho_t(0) + \frac{d}{dE}\rho_t(0)E + \mathcal{O}(2), \tag{7}$$

to replace $\rho_t(E)$ in the integral in Eq. (6). In the zeroth order approximation, the integral can now be analytically solved. This is a reasonable approximation under the assumption that ρ_t is sufficiently flat, or—more precisely—that $E(d/dE)\rho_t(0) \ll \rho_t(0)$. In this case, we can perform a background removal by simple subtraction:

$$\rho_S \propto M_{on}(V) - \frac{M_{on}(0)}{M_{off}(0)}M_{off}(V) + C. \tag{8}$$

The prefactor $M_{on}(0)/M_{off}(0)$ of the off spectrum will generally be close to 1 if on and off spectra are recorded under similar stabilization conditions. This method determines ρ_S up to a factor and an additive constant and as we will see later, it is surprisingly successful. For metal tips, the variations in the LDOS at the Fermi level are relatively small thus the condition for the validity of this scheme $E(d/dE)\rho_t(0) \ll \rho_t(0)$ is for small bias voltages satisfied.

III. DECONVOLUTION

A more sophisticated way to perform background subtraction is to deconvolute the on spectrum with the off spectrum. This is achieved by numerically solving the integral Eq. (6) for ρ_S. We can replace the tip LDOS in Eq. (6) by application of Eq. (4) giving

$$M_{on}(V) - \frac{M_{on}(0)}{M_{off}(0)}M_{off}(V)$$
$$= \frac{C_{on}}{C_{off}\bar{\rho}_{S0}}\int_0^{eV} M_{off}(eV - E)\frac{d}{dE}\rho_S(E)dE. \tag{9}$$

Apart from the constants C_{on}, C_{off}, and $\bar{\rho}_{S0}$, this equation only depends on the measured spectra M_{on} and M_{off}. It can be solved in a discrete form, giving an algorithm for numerical background removal

$$\frac{d}{dE}\tilde{\rho}_S(n\Delta V) = \frac{M_{on}(n\Delta V) - \tilde{M}_{off}(n\Delta V) - \sum_{k=0}^{n-1}\tilde{M}_{off}[(n-k)\Delta V]d/dE\tilde{\rho}_S(k\Delta V)e\Delta V}{M_{on}(0)\Delta V}, \tag{10}$$
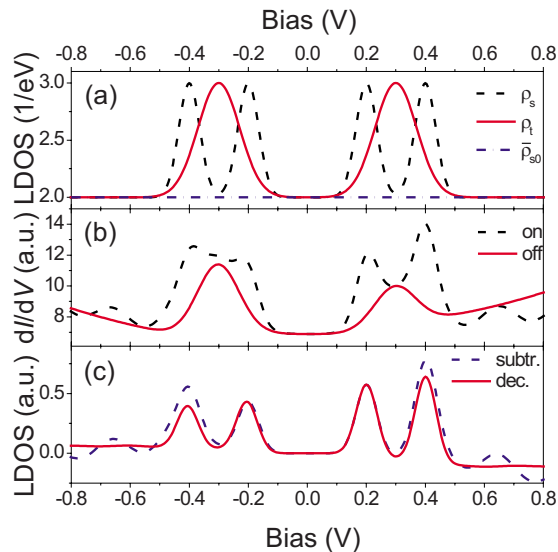
FIG. 2. (Color online) Background subtraction and tip deconvolution for simulated STS spectra. (a) Initial LDOS of the tip of the sample at the position of the object of interest and of the clean surface. (b) Calculated dI/dV signal for a lock-in modulation of 10 mV (with open-feedback loop) for on and off specta. (c) Spectrum after simple background subtraction and full deconvolution (dec.).
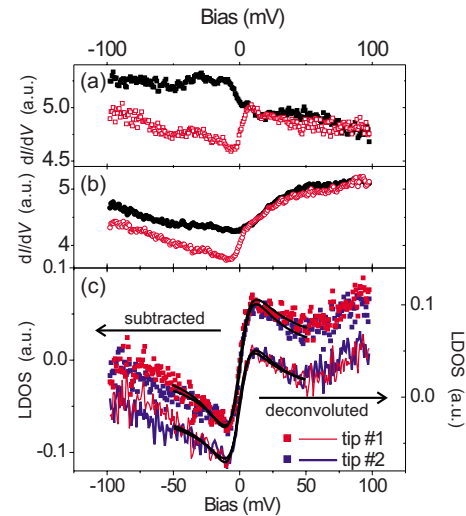

FIG. 3. (Color online) Background subtraction for the Kondo resonance of a single cobalt adatom on Cu(100): (a) and (b) show spectra recorded on (open symbols) and off (full symbols) with two different tips, in (c) the spectra after background removal by simple subtraction and full deconvolution for both tips are plotted, spectra are vertically shifted for clarity. In addition, fits of a Fano function are shown (solid black lines).

where $\tilde{M}_{off}(E) = M_{off}(E)M_{on}(0)/M_{off}(0)$ and $\tilde{\rho}_S(V) = \rho_S(V)/\rho_S(0)$. Apart from an additive and a multiplicative constant, the only remaining parameter is the initial value $(d/dE)\tilde{\rho}_S(0)$, which will for metal surfaces be close to zero for the same reasons as discussed above. It can be determined by requiring the resulting LDOS to be differentiable at the Fermi energy. The final step in the algorithm consists of a numerical integration to obtain $\tilde{\rho}_S$.

IV. COMPARISON

First, we will consider simulated STS spectra and show how the two methods perform to recover the initial sample LDOS. In the second part, experimental data will be presented to show how background removal improves the quality and reproducibility of STS spectra. The STS spectra have been simulated using a tip LDOS consisting of two Lorentzians and a sample LDOS which is composed of four Lorentzian peaks. The LDOS of the clean surface is assumed to be constant. Equations (1) and (2) have been employed assuming $T = 0$ K but taking into account lock-in broadening with a modulation of 10 mV$_{p.p.}$.[12,13] The widths and positions of the peaks differ between tip and sample LDOS, both are plotted in Fig. 2(a). The on spectrum [Fig. 2(b)] shows a complex structure with dominant features due to the tip LDOS. These artifacts consist of dips and peaks, dominantly at the positions of the features in the tip LDOS but there are also satellite features at higher energies. The results of both the simple background subtraction and the full deconvolution are depicted in Fig. 2(c). While the simple background subtraction performs well on the main features, it fails to remove the satellites caused by the tip spectrum. The situation becomes considerably better for a full deconvolution, which also suppresses the satellites. Since the described methods for back-

ground subtraction do not correct the variation of the transmission probability with energy, the peak heights of the original LDOS are not recovered.

For a more realistic tip LDOS, the simple background subtraction performs almost as well as the deconvolution algorithm. This can be seen from the following experimental examples. Although the algorithms have been derived for elastic tunneling, we will show that they can equally be applied to inelastic tunneling features originating from excitations within the tunneling gap. The spectra have been measured using a homebuilt low temperature STM operating in ultrahigh vacuum (UHV) with standard UHV sample preparation and *in situ* transfer of the sample to the STM. The STM operates at 6 K. To record the spectra, the dI/dV signal is detected by a lock-in technique. As a substrate, we use the Cu(100) surface, where for small bias voltages, the LDOS is featureless.

The first object we will consider is a single cobalt adatom on the Cu(100) surface, the preparation and experimental details have been described elsewhere.[14] The cobalt adatoms are magnetic impurities and, at low temperature, the Kondo effect leads to the formation of a resonance in the LDOS at the Fermi level.[15] Figures 3(a) and 3(b) show a set of on and off spectra recorded with two different tips on the same cobalt adatom, where different means that the very end of the tip has been modified by dipping it into the surface. The two different tip apex configurations lead to on spectra that will not allow a reliable line-shape analysis without accounting for the tip LDOS, although qualitatively similar features are present at the Fermi energy. After background removal by both subtraction and deconvolution, the artifacts due to the tip have disappeared as can be seen by the comparison of the curves in Fig. 3(c). Small differences between the deconvoluted and the subtracted spectra are found. The full deconvolution yields a slightly better suppression of the influence of the tip in the energy range between 0 and
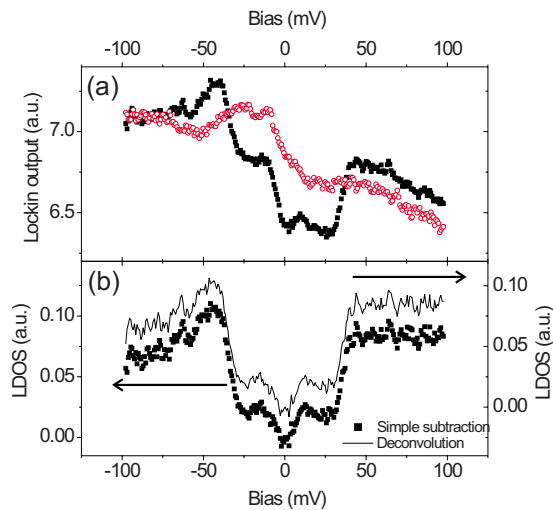
FIG. 4. (Color online) Experimental example for background subtraction: (a) spectrum acquired on top of a CO molecule on Cu(100) (open symbols) and on the clean surface about 1 nm away from the molecule (full symbols), (b) background subtracted spectrum using the simple method [Eq. (8)], and a full deconvolution [Eq. (10)].

50 meV than the simple subtraction. This example shows the potential of background removal: the spectra recorded with the two different tips are almost identical after correction for tip artifacts. For comparison, in Fig. 3(c), fits of Fano functions to all four spectra are plotted. The observed line shape of the Kondo resonance is in excellent agreement with the fits—which is in contrast to the raw spectra shown.

The second example deals with the vibrational excitations of a CO molecule[2] demonstrating that the same methods are applicable in the case of inelastic excitations. The on spectrum shown in Fig. 4(a) has been acquired on a single CO molecule, while the off spectrum has been recorded on the clean surface a few nanometers away from the CO molecule. The IETS spectra are expected to show steps in the conductance due to inelastic tunneling processes.[2,16] The steps should be symmetric with respect to the Fermi energy. The on and the off spectra both reveal a variety of features: they are both tilted by an almost linear background and the off spectrum exhibits a feature around −25 mV. In the raw on spectrum, the vibrational features can be readily recognized, but they are obscured by tip-related structures. In the background subtracted spectra shown in Fig. 4(b), only the vibrational features are found, while the tip-related structures are gone. The energies of the vibrational modes at 4 and

35 meV are consistent with previous work[16] and the spectrum shows the expected symmetry. The numerical deconvolution does not improve the spectrum compared to the simple subtraction method, which is to be expected since the condition for the simple subtraction to perform well, i.e., $E(d/dE)\rho_t(0) \ll \rho_t(0)$ is fulfilled.

V. CONCLUSION

We have presented two background removal algorithms for STS spectra. These algorithms require data taken with the same tip on a surface area where the LDOS is constant or known. It is found that a full deconvolution algorithm performs only slightly better than a simple background subtraction. The reason for the success of the simple method can be found in the condition for its validity. Since the variation of the LDOS of a metal is typically rather small compared to the total LDOS for energies close to the Fermi energy, this condition is met. So, in most cases, a simple subtraction of the background spectrum will be sufficient to recover the sample LDOS from the tunneling spectra thereby minimizing the influence of the tip. This has been demonstrated on experimental data for the Kondo resonance of a cobalt adatom on Cu(100) and for an inelastic tunneling spectrum recorded on a CO molecule in cases where the tip LDOS obscures spectral features due to the adsorbate.

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